CHARACTERIZATION AND PROPERTIES OF LINEAR LOW DENSITY POLYETHYLENE/POLY(VINYL ALCOHOL) BLENDS

by

RAZIF BIN MUHAMMED NORDIN

Thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy

AUGUST 2011

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UNIVERSITI SAINS MALAYSIA

JULY 2011

DEDICATION

This work is dedicated to my beloved

ACKNOWLEDGEMENTS

First and foremost I would like to offer my unreserved gratitude and praises to Almighty Allah for His generous blessing and the undying strength bestowed upon me during the course of this research.

I wish to acknowledge the support of Universiti Teknologi MARA, Universiti Sains Malaysia and JPA for providing the opportunity to undertake this work. My special acknowledgement to my main-supervisor, Professor Dr. Hanafi Ismail for his constant encouragement, guidance and assistance during my period of study. The constant guidance and assistance offered by my co-supervisor, Assoc. Prof. Dr. Zulkifli Ahmad and Assoc. Prof. Dr. Azura Rashid are gratefully acknowledged.

Special thanks to the Dean and all the staff in School of Materials and Mineral Resources Engineering USM for their co-operation and help. I would also like to forward my gratitude to technical staff namely En. Segar, En Rashid, En Azam, En. Rokman, En. Faizal, En Suhaimi and Pn. Fong.

My special appreciation goes to my colleagues Nik Noriman, Kak Zurina, Ragunathan, Kahar, Sam Sung and Basree for their encouragement through this research work. My sincere thanks are also extended to all my postgraduate colleagues namely Faizal, Amid, Bisrul, and all the numerous friends whose names have not been mentioned, it was nice knowing you all.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

T_c	Crystallization transition temperature
T_m	Melting temperature
ΔH_f	Heat of fusion
X_c	Degree of crystallinity
php	Part per hundred polymer
rpm	Revolution per minute
^oC	Degree Celsius
kGy	Kilo Gray
Bsp	Bahagian perseratus polimer

LIST OF ABBREVIATION

BHT	Buthylated hydroxytoluene
DCP	Dicumyl peroxide
DSC	Differential scanning calorimetry
LLDPE	Linear low density polyethylene
PE	Polyethylene
PVA	Poly(vinyl alcohol)
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
TMPTA	Trimethylolpropane triacrylate

PENCIRIAN DAN SIFAT-SIFAT ADUNAN POLIETILENA LINEAR BERKETUMPATAN RENDAH /POLI(VINIL ALKOHOL)

ABSTRAK

Kesan komposisi adunan, agen sambung-silang, radiasi alur elektron dan gabungan radiasi serta agen sambung silang ke atas sifat-sifat adunan polietilena linear berketumpatan rendah/poli(vinil alkohol) telah dikaji. Sambung silang disediakan menggunakan asid maleik dan 3-(trimetoksisilil)propil metakrilat sebagai agen sambung silang dan dikumil peroksida (DCP) sebagai pemula, sementara trimetilolpropana triakrilat (TMPTA) sebagai agen sambung silang yang dipilih untuk proses radiasi. Adunan telah disediakan dengan menggunakan pencampur dalaman Haake Rheomix Polydrive pada suhu 150 ºC dan kelajuan rotor 50 rpm. Sistem adunan meliputi komposisi yang berbeza iaitu 90/10, 80/20, 60/40, 50/50 dan 40/60 LLDPE/PVA (bsp/bsp). Keputusan menunjukkan sifat-sifat tensil berkurangan dengan peningkatan komposisi PVA, disebabkan oleh tiada keserasian antara komponen LLDPE dan PVA. Keputusan kalorimeter imbasan pembeza (DSC) dan morfologi menunjukkan adunan adalah tidak terlarutcampur untuk semua komposisi. Namun demikian, sambung silang secara kimia menggunakan asid maleik dan 3-(trimetoksisilil)propil metakrilat telah meningkatkan keserasian, kestabilan terma dan sifat-sifat tensil adunan LLDPE/PVA. Pembentukan sambung silang dibuktikan menggunakan FTIR dan diukur berdasarkan kandungan gel. Kehadiran sambung silang nyata sekali mengubah morfologi adunan LLDPE/PVA. Keputusan ini mematuhi teori yang menyatakan bahawa sambung silang meningkatkan keserasian bagi adunan tidak boleh campur. Dengan mengenakan

radiasi alur elektron ke atas adunan LLDPE/PVA pada dos yang berbeza, iaitu 50, 100, 150, 200 dan 250 kGy telah meningkatkan sambung silang adunan. Sambung silang yang dipengaruhi oleh radiasi meningkat dengan peningkatan dos radiasi dan menyebabkan peningkatan pada sifat-sifat tensil, sifat-sifat terma dan keserasian adunan. Sifat-sifat terbaik adunan LLDPE/PVA dicatat pada dos penyinaran 200 kGy. Penggunaan agen sambung silang TMPTA telah meningkatkan lagi sambung silang ini dan menyebabkan peningkatan dalam keserasian, sifat-sifat terma dan kekuatan tensil.

Berdasarkan keputusan kekuatan tensil dan pemanjangan pada takat putus, 3-(trimetoksisilil)propil metakrilat merupakan agen sambung silang yang terbaik untuk adunan LLDPE/PVA berbanding asid maleik atau TMPTA. Oleh itu, adunan LLDPE/PVA dengan dan tanpa penambahan 3-(trimetoksisilil)propil metakrilat dipilih untuk kajian degradasi dengan mendedahkannya di bawah cuaca semula jadi selama enam bulan. Keputusan menunjukkan adunan dicampur dengan 3-(trimetoksisilil)propil metakrilat memberi nilai retensi kekuatan tensil dan pemanjangan pada takat putus yang paling rendah berbanding adunan tanpa 3-(trimetoksisilil)propil metakrilat terutamanya dengan peningkatan masa pendedahan dan kandungan PVA. Mikrograf SEM (mikroskop imbasan elektron) untuk adunan yang didedahkan di bawah cuaca semula jadi menunjukkan permukaan retak yang berterusan dan kulat tumbuh pada kedua-dua adunan sebagai bukti proses fotodegradasi dan biodegradasi telah berlaku.

CHARACTERIZATION AND PROPERTIES OF LINEAR LOW DENSITY POLYETHYLENE /POLY(VINYL ALCOHOL) BLENDS

ABSTRACT

The effect of blend ratio, crosslinking agent, electron beam irradiation and the combination of irradiation and crosslinking agent on the properties of linear low density polyethylene/poly(vinyl alcohol) blends were investigated. The crosslinking was prepared using maleic acid and 3-(trimethoxysilyl)propyl methacrylate as crosslinking agents and dicumyl peroxide (DCP) as initiator, while trimethylolpropane triacrylate (TMPTA) was crosslinking agent chosen for irradiation process. Blends were prepared by melt mixing in an internal mixer, Haake Rheomix Polydrive at temperature and rotor speed of 150ºC and 50 rpm respectively. Blend systems covered various compositions viz. 90/10, 80/20, 60/40, 50/50 and 40/60, of LLDPE/PVA (php/php). Results showed that the tensile properties decreased with increases in PVA content, these were due to incompatibility between LLDPE and PVA components. Results on differential scanning calorimetry (DSC) and morphology revealed that the blend were immiscible at all blends ratios. Meanwhile, chemical crosslinking through maleic acid and 3-(trimethoxysilyl)propyl methacrylate has enhanced the compatibility, thermal stability and tensile properties of LLDPE/PVA blends. The formation of crosslinking was proved by FTIR and quantified with gel content. The presence of crosslink's significantly alters the morphology of LLDPE/PVA blends. These findings follow the theory which stated that the crosslinking formation enhanced the compatibility of immiscible blends. The introduction of electron beam irradiation

on LLDPE/PVA blends at different dosage viz. 50, 100, 150, 200 and 250 kGy has enhanced the irradiation-induced crosslinking. Irradiation-induced crosslinking increased with the increase in irradiation dose and lead to the improvement in tensile properties, thermal properties and compatibility of the blend. The best properties of LLDPE/PVA blends was recorded at irradiation dose of 200 kGy. The incorporation of crosslinking agents, TMPTA has further enhanced the irradiation-induced crosslinking and lead to the improvement of compatibility, thermal stability and tensile properties.

Based on tensile strength and elongation at break results, 3-(trimethoxysilyl)propyl methacrylate showed the best crosslinking agent for LLDPE/PVA blends compared to maleic acid and TMPTA. Therefore, LLDPE/PVA blends with and without additional of 3-(trimethoxysilyl)propyl methacrylate was chosen for degradation studied by exposing it under natural weathering for six months. The results showed blends incorporated with 3-(trimethoxysilyl)propyl methacrylate give lower value on tensile strength and elongation at break retention compare to blends without 3-(trimethoxysilyl)propyl methacrylate particularly with increasing exposure time and PVA content. SEM micrographs of exposed blends under natural weathering showed continuous cracks formation and fungi growth on the surface of both blends as an evidence of photodegradation and biodegradation process have occurred.

CHAPTER 1

INTRODUCTION

1.1 Biodegradable Plastics: The Trend

Over the last 50 years, polymer industries have grown substantially because they are made from inexpensive, renewable and readily available materials. Polymer products are used such as in constructions, communication, transportations, textiles, packaging and medical components. Polymer products are either made of from a pure synthetic or natural polymers or combination between both polymers.

The projected life-span of polymer products varies from several months for packaging products, and to over 50 years for construction components. In United States alone, about 50 millions tons of synthetic polymers were consumed every year (Charles, 2008). Of this, 64% accounts for the packaging products are made of polyethylene. This makes linear low density polyethylene as the mostly used in packaging industry and the most important synthetic polymer today (Santana and Manrich, 2003, Satapathy et al., 2006, Jose et al., 2007, Ojeda et al., 2009).

Since most of the packaging products are "throwaway" items, the amount of waste plastics generated is enormous. Statistically, in United Sates, the amount of waste plastic bags accumulates at a rate of 100 billion each year (Vaughn, 2009). Earlier most of the waste plastics were buried in the landfill. This leads to serious environment effect as most of them are non biodegradable (Singh and Sharma, 2008). At the same time, the landfilling practice is going to be banned in the near future due to public health reasons (http://www.hazawaste.unabridged.pdf). This

makes waste management an urgent problem that needs environmental compatibility and eco-friendly solution.

To minimize waste plastics, conventional techniques like recycling and incineration were used. However, these techniques had serious limitations such as:

a. Recycling is only practical for scrap plastics by manufacturing, while collection of plastic waste for recycling is expensive. Especially, when plastics are contaminated with soil, food, or other chemicals, recycling of these plastics waste is rather difficult. As such, only 1% of plastic waste is recycled in the United States in 2008 (Vaughn, 2009).

b. Incineration of plastics waste is less attractive due to high capital cost and may produce carcinogens such as dioxin. This process also consumes a lot of energy and generates greenhouse gases such as carbon dioxide (Lea, 1996) and expensive.

Therefore, a lot of effort has been focused in recent years to develop environmentally compatible plastic products that possess biodegradability characteristics. Several approaches had been considered in accelerating biodegradation process such as:

a. Synthetic polymer with additives

   Incorporation of photosensitive (Ratanakamnuan and Ong, 2006; Harada et al., 2007) and pro-oxidant (Johnson et al., 1993; Shah et al., 1995; Koutny et al., 2006; Roy et al., 2007; Fontanella et al., 2010) additives induced degradation process of polymer by photo-

oxidation. Polymers incorporated with this additives were classified as oxo-degradable polymers (Chiellini et al., 2006a).

b. Synthetic polymer with hydrolysable backbones

Polymers with hydrolysable backbones are fully biodegradable under suitable conditions. Examples of polymers with hydrolysable backbones are aliphatic polyesters such as polylactic acid (Drumright et al., 2000; Kumar et al., 2010), polycaprolactone (Teramoto et al., 2004; Vašková et al., 2008), polyhydroxybutyrate (Kim et al., 2000, Çetin 2009, Volova et al., 2010) and so on. These polymers are often too expensive for nonmedical use (Chen et al., 2007; Vašková et al., 2008; Cottam et al., 2009; Sambha'a et al., 2010).

c. Synthetic polymers with carbon backbones

Polymer with carbon backbones, such as vinyl polymers is fully biodegradable (Katsura and Sasaki, 2001). However, photo-degradation is essential for degradation process of vinyl polymers.

d. Biodegradable polymers from renewable resources

Biodegradable polymers obtained from renewable resources such as polysaccharides (Glenn and Orts, 2001; Avella et al., 2005; Senna et al., 2007), proteins, and bacterial polymers have attracted significant researches.

For these bio-plastics, prices is by far the most important issue since they should able to compete with low cost synthetic commercial polymers. In this regard, blending biodegradable polymers either natural or synthetic with commercial

plastics will enlarge the range of applicability of these materials in packaging applications.

1.2 Problem Statements

1.2.1 Biodegradable Polyethylene/Starch Blends

Research on polyethylene/starch blends started in the early 1970's with the aims to enhance the biodegradability of polyethylene. Starches are renewable natural polymer, inexpensive, abundant and fully biodegradable (http://ec.europa.eu/agriculture/eval/reports/amidon/chap1.pdf). Furthermore, starch can be easily found in a variety of plants such as corn, cassava, sago, rise and banana (Smith, 2005a). However, the tensile properties (tensile strength and elongation at break) of polyethylene/starch blends decreased with increasing starch content (Park et al., 2002). This is due to starch consist of two structural molecules of amylose and amylopectin that tend to agglomerates in hydrophobic polymers.

The tensile properties of polyethylene/starch blends were enhanced with incorporation of compatibilizer (Tanrattanakul and Panwiriyarat, 2009; Majid et al., 2010). However biodegradation rate of the blends are significantly decreased (Bikiaris et al., 1998; Ratanakamnuan and Aht-Ong, 2006) due to crosslinking formed between polyethylene and starch. Furthermore, the amount of compatibilizer must be used in a large quantities, because some of it will react with plasticizer. The starch used only thermally processable when plasticizer such as glycerol is added (Fakirov and Bhattacharyya, 2007; Schlemmer and Sales, 2010). The presence of plasticizer in polyethylene/starch blends can caused loss of tensile

properties with time due to dimensional instability resulted from leaching of plasticizer (Soest et al., 1994).

Even though, starch is suitable for partially replace polyethylene, but there is drawback since starches are food items. In the recent global food crisis (http://www.ifpri.org/publication/international-agricultural-research-food-security-poverty-reduction-and-environment), it is best to avoid incorporating starch in polyethylene. Hence starch needs to be replaced with synthetic biodegradable polymer.

1.2.2 Biodegradable Poly(vinyl alcohol)/Starch Blends

Poly(vinyl alcohol) (PVA) is important synthetic biodegradable polymer with excellent gas barrier properties, high strength, tear, and flexibility (Ibrahim et al., 2007). However, it has poor dimensional stability due to high moisture absorption, and relatively expensive compared to other synthetic nonbiodegradable polymers. It is therefore, generally blended with agro-resource based on polysaccharides, particularly starch to reduce manufacturing cost.

Blending PVA with starch has resulted in more moisture resistant and accelerates degradation process of the blends (Russo et al., 2009; Han et al., 2009). However, the properties of the blends deteriorated as starch content in the blend increased, owing to a poor compatibility between the two components and phase separation during the blend preparations.

The compatibility between poly(vinyl alcohol) and starch was further improved by addition of suitable plasticizers (Siddaramaiah et al., 2004; Sreedhar et al., 2006), crosslinking agents (Sin et al., 2010; Yoon et al., 2006; Krumova et al., 2000), fillers (Jia et al., 2007; Dean et al., 2008; Peng et. al., 2005) and compatibilizers (Guohua et al., 2006; Nath et al., 2010). The properties of PVA/starch blends can further enhanced by coating with synthetic non-biodegradable or biodegradable polymers.

Otey et al., (1974) designed PVA/starch blends for agricultural applications. The resulting films were then coated with a non-biodegradable synthetic polymer with PVC in order to improve their tensile strength. However, the biodegradation tendency of these films were not been investigated. Lahalih et al. (1987) then improved Otey et al., (1974) works by coating PVA/starch films with biodegradable synthetic polymer, poly(vinyl acetate) layers which resulted on strong and flexible clear films. The tensile strength, elongation at break and biodegradation properties of films was increased with addition of ethylene glycol, starch, and urea. Coated PVA/starch film, however, has a drawback because it involved higher additional cost.

PVA/starch blends were frequently prepared in solution form due to low thermoplasticity of PVA at melting temperature (Alexy et al., 2002) which was not acceptable because it involved in high processing cost and low efficiency of solution processing compared to thermoplastic processing. Furthermore, PVA/starch blends are too weak for daily used when expose to humidity. Mao et al., (2000) reported that the strength of PVA/starch decreased by 60% as the relative humidity increased

form 30 to 93% (Moa et al., 2000). In oder to increase the applications of PVA, the moisture absorptions need to be reduced together with the processing according to thermoplastic technique. This can be achieved by blending PVA with commercial polymer such as polyethylene, polypropylene, polyvinyl chloride and so on.

From the economic point of view, polyethylene/PVA blends are likely acceptable because polyethylene will lower production cost and give higher water resistance properties (Satapathy et al., 2006; Santana and Manrich, 2003; and Lui et al., 1999) when blended with PVA. Unfortunately, the preparation of polyethylene/PVA blends by thermoplastics processing was not reported widely. Lui et al., (1999) showed that starch/PVA/polyethylene blends are processable through thermoplastic technique with incorporation of plasticizers. However, it is difficult to improve mechanical properties of plasticizers blends because plasticizers will hindrance the chemical interaction between the blends and compatibilizer (Soest et al., 1994).

The main aim of blending polyethylene with poly(vinyl alcohol) is to develop a new biodegradable polymer with intermediate properties of both polymers. However, one of the crucial factors governing the properties of the multi-component polymer is phase separation behavior (compatibility between the phases) which contributes from adhesion between the non polar polyethylene and polar poly(vinyl alcohol), which makes it difficult to produce blends with the desired properties by simple blending process.

Within this work, the area of research has undergone rapid diversification. It ranges from the use of compatibilizer and coupling agent of incompatible polymers to foster compatibility which improved the properties of LLDPE/PVA blends and degradation process of selected blends. All these have been done in order to produce a new range of polymer blend.

1.3 Objectives of the Study and Organization of the Thesis

1.3.1 Objectives of this Study

The main objective of this study is to investigate the possibility of producing a new thermoplastic material from the blend of linear low density polyethylene (LLDPE) and polyvinyl alcohol (PVA) without the presence of plasticizer. The studies on the effect of blend ratios and natural weathering with some process modifications such as compatibilizer (maleic acid and silane coupling agent), electron beam (EB) irradiation and irradiation with the existence of crosslinking agent/coagent (TMPTA) on the characteristic and properties of LLDPE/PVA blends were evaluated.

The specific objectives in this study are:

- To study the effect of blends ratio and different additives on processability of LLDPE/PVA blends.
- To quantify the degree of crosslinking of LLDPE/PVA blends through gel content and verify the gel with Fourier transform infrared (FTIR).
- To determine the thermal properties (melting temperature, degree of crystallinity and thermal stability) of LLDPE/PVA blends.

- To measure the tensile properties (tensile strength, elongation at break and Young's modulus) of LLDPE/PVA blends.
- To determine the morphology of LLDPE/PVA blends.
- To evaluate the effect of natural weathering on LLDPE/PVA blends.

1.3.2 Organization of the Thesis

There are ten chapters in this thesis and each chapter gives information related to the research's interest.

- **Chapter 1** contains the introduction of the thesis. Its' covers a brief introduction about research background, a problem statement, objectives of the project and organization of the thesis.
- **Chapter 2** contains the literature review. Its' covers the fundamental of polymer blends and also a general overview about the process modification on the polymer blends.
- **Chapter 3** contains the information about the materials specification, equipments and experimental procedures used in this study.
- **Chapter 4** discusses the effect of blend ratios on LLDPE/PVA blends.
- **Chapter 5** discusses the effect of maleic acid on LLDPE/PVA blends through *in situ* crosslinking.
- **Chapter 6** discusses the effect of 3-(trimethoxysilyl)propyl methacrylate on LLDPE/PVA blends through *in situ* crosslinking.
- **Chapter 7** discusses the effect of different irradiation dose on the irradiation-induced crosslink of LLDPE/PVA blends.
- **Chapter 8** discusses the effect of and trimethylolpropane triacrylate (TMPTA) the irradiated blends

- **Chapter 9** discusses the effect of natural weathering on the LLDPE/PVA blends with and without incorporation of 3- (trimethoxysilyl)propyl methacrylate.
- **Chapter 10** concludes the above findings and assessment was made to evaluate the achievement of the objectives.

CHAPTER 2

LITERATURE REVIEW

2.1 Polymer Blends

The technology of polymer blends is a major area of research and development in polymer science over the past three decades, based from the number of publications and patents. The current worldwide market volume for polymer blends is estimated to be more than 700,000 metric ton/year, with an average growth rate of 6% to 7%. The polymer blends market has slackened due to the global economic slowdown (http://www.researchandmarkets.com). However, the demand for polymer blends is expected to be maintained due to the possibility to adjust the cost-performance balance and tailoring the technology to make products for specific end-use applications (Utracki, 2003).

Utracki (2002) defined polymer blend as a mixture of at least two macromolecular substances, polymer or copolymer, in which the ingredient content is above 2 wt%. This definition does not relate to mixing technology between the components (Paul and Newman, 1978). Therefore, polymer blends include blends prepared through mechanical blending, chemically modified blends through compatibilization, reactive blending, grafted and block polymers, and interpenetrating networks.

The advantages of polymer blends versus developing new polymeric structures have been well documented (Utracki, 2002). The ability to combine

existing polymers into new compositions with commercial properties offers several advantages of polymer blends over development of new monomers/polymers such as:

a. Providing materials with full set of desired properties at lower prices. Blending of commercially available polymers is more cost effective method of developing a new product that meets the market requirements, as opposed to developing a totally new polymer that generally involves relatively high research, development and capital cost.

b. Polymer blends can fill the cost-performance gaps in the existing commercial polymers. Several properties can be uniquely combined in a blend that a single resin often cannot provide.

c. Offering the means for industrial and/or municipal plastics waste recycling (Chanda and Roy, 2006a) and etc.

Blend also benefits manufacturer by offering:

a. Improved processability, product uniformity, and scrap reduction.

b. Quick formulation changes. Blends can be formulated, optimized and commercialized generally at a much faster rate than new polymers, provided there are no major barrier for the compatibility between the components.

c. Plant flexibility and high productivity. Polymer blending can be done at a relatively low cost using an extruder. Production of new polymers, on the other hand, requires capital intensive plants and reactors that must operate on a reasonably large scale for reasons of economics etc.

2.1.1 Mechanical Blending

In plastic processing the terms mixing, blending and compounding have different meanings. Mixing indicates the physical act of homogenization, blending usually indicates preparation of polymer blend and alloys, while compounding is the incorporation of additives into polymeric matrix (Utracki, 2002).

Mechanical blending has become one of the commercially essential ones. The preparation methods of mechanical blends are melt mixing, dissolution in co-solvent followed by film casting, latex blending, fine powder mixing and use of monomer as a solvent with another blend component and subsequently polymerization. Between these methods, melt mixing predominates. This is due to many advantages offered this method than other methods. Some of the melt mixing advantages are (Utracki, 1990; Coran, 2001), (a) simplicity of technology (b) short processing time (c) minimum operator skill (d) avoid contamination (such as from solvent) (e) cost benefits associated with above factors

2.1.2 Compatibilization of Polymer Blends

In general, most polymer blends not only immiscible in nature but are also mechanically incompatible (Rana et al., 1998). Fortunately, even immiscible blends proved to be mechanically compatible provided adequate adhesion between the phases exists. To achieve useful properties, compatibilization method must be employed for these blends. According to Fink (2005), compatibilization of immiscible blends can be produced by: (a) the addition of compatibilizer before or during the blending process, (b) adjustment of viscosity ratios to favor rapid

formation of the desired phase morphology during mixing, (c) i*n situ* formation of compatibilizer during the blending process, and (d) introduction of crosslinking in the blends.

Compatibilization is a process of modification of interfacial properties of an immiscible polymer blend, leading to creation of polymer alloy. A polymer alloy in turn is defined as an immiscible polymer blend having a modified interface and/or morphology. Thus, all polymer alloys are blends, but not all polymer blends are alloys (Brown, 2002). The general relationship between blends and alloys (Chanda and Roy, 2006b) is shown in Figure 2.1.

Alloys performance depends on the interfacial agent. The interfacial agent improved mechanical compatibility by achieving interfacial adhesion between polymers phase. Thus, interfacial agent act as "surfactant" that concentrates at the interface and stabilizes the morphology of polymer blends. This stabilization prevents agglomeration which is one of the major problems due to small particle size dispersions by shearing uncompatibilized blends. Therefore, a successful compatibilization process must be accomplished as follows: (a) reduce the interfacial tension, and produce finer dispersion, (b) stabilize the morphology against thermal or shear effects during the processing steps, and (c) enhance interfacial adhesion between the phases in the solid state for better the stress transfer hence improving the mechanical properties of the product (Utracki, 2002).

The compatibilization approaches include: (a) addition of a small quantity of a third component that either is miscible with both phases, or it is a copolymer

whose one part is miscible with one phase and another with the other phase, (b) addition of a copolymer whose one part is miscible with one phase and another part with the other phase, (c) addition of a large amount of a core shell copolymers that behaves like a multi-purpose compatibilizer-cum-impact modifier, (d) reactive compatibilization, designed to enhance the domain interactions and generate finer morphology by creating chemical bonds between the two homopolymers during the compounding or forming processes and etc (Robenson, 2007).

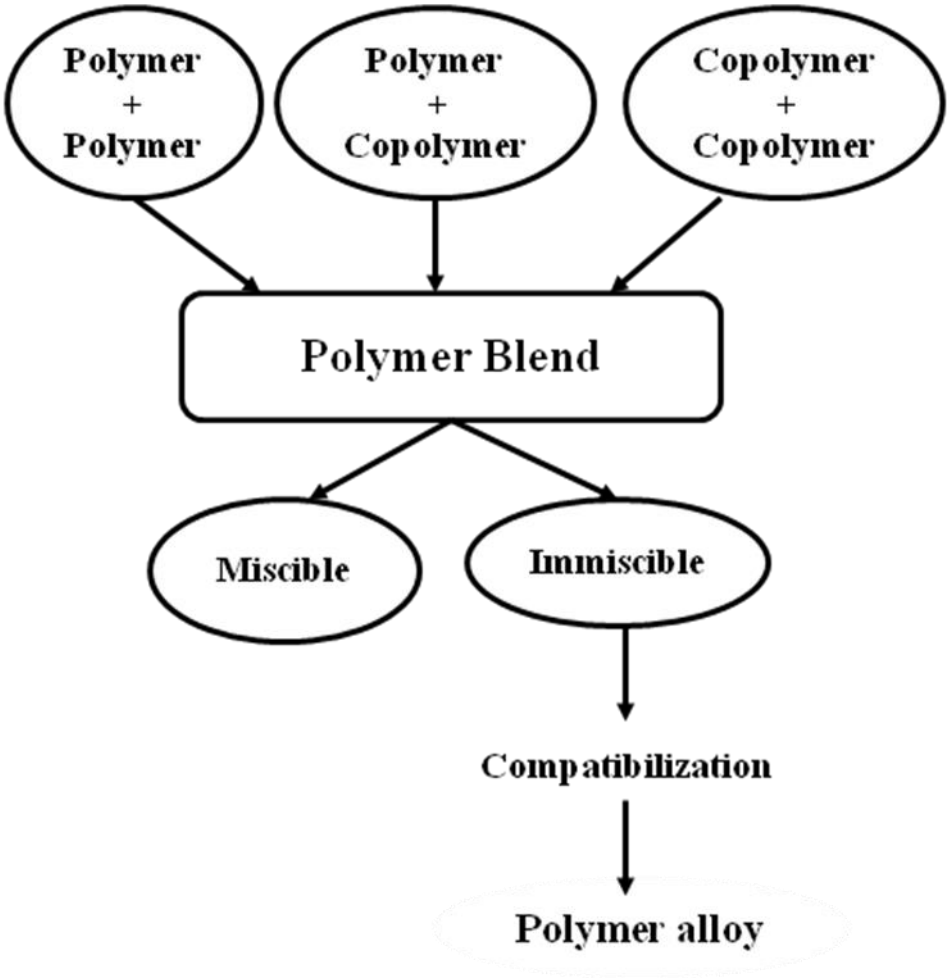

Figure 2.1 Schemetic representation of the general relationship between polymer blends and alloys (Chanda and Roy, 2006b)

2.1.3 Reactive Compatibilization

Reactive compatibilization technique allowed in-situ formation of graft or block copolymers of blend. This technique proved to be effective and utilized by many researchers as well as in commercial blends. The concept of reactive compatibilization involves the incorporation of a reactive site onto a polymer chain identical to one blends component capable of reacting with other polymeric component. The resultant graft copolymer will concentrate at the interface and reduce the interfacial tension. This improved dispersion, domain size reduction, and also improved the mechanical properties over the binary blend. Furthermore, reactive compatibilization may involve in chemical bonding between polymers resulting in significant increase of the molecular weight at the interface (Utracki, 2002).

Reactive compatibilization has at least two advantages, mostly economical which are: (a) the copolymer is made as needed during the melt blending process and separate commercialization of a copolymer is not required, (b) the copolymer is formed directly at the interface between the immiscible polymers where it is needed to stabilize the develop phase morphology. However, the main disadvantage of reactive blending resides in the need to have reactive functional groups on the polymers to be compatibilized.

2.2 Water-soluble Biodegradable Polymeric Materials

Water-soluble polymeric materials constitute a diverse class of macromolecules, and may be classified according to their source (Chandra and Rustgi, 1998):

a. Natural origin, better known as biopolymers (polysaccharides, proteins, polypeptides polynucleotides, polyphosphates, and polysilicates), directs and modulates the complex functional processes fundamental to living organisms,

b. Semi synthetic origin, comprising chemically modified natural polymers (formerly known as artificial polymers). Most natural polymers must be submitted to functional group manipulations in order to allow processing and conversion to useful items,

c. Synthetic origin, based on feed-stocks derived from fossil fuel and renewable resources. The latter are gaining increased attention for industrial development, driven by the principles of sustainability.

Water-soluble polymers are suitable for a wide range of applications in different industrial ranging from food, textiles, leather, coatings, paper, healthcare, oil recovery, waste water, treatment biomedical to pharmaceutical fields. These represent an enormous commercial impact with minimal environmental concern.

The performance of water-soluble polymeric materials depends on the balance between the functional groups (structure, relative concentration, and position in the repeating unit) and the overall hydrocarbon (hydrophobic) content of the repeating units (http://www.snf-group.com/IMG/pdf/Water_Soluble_ Polymers_E.pdf). Their arrangement in homopolymer or copolymer structures represents a key aspect in affecting water solubility. Typical examples of the various classes of water-soluble to synthetic polymers are listed in Table 2.1

Table 2.1 Categorization of water-soluble synthetic polymers (http://www.snf-group.com/ IMG/pdf/Water _Soluble_Polymers_E.pdf)

Non Ionic	Cationic	Anionic
Poly(acrylamide)	Poly(diallyldimethyl ammonium chloride)	Poly(acrylic acid)
Poly(N-isopropylacrylamide)	Poly(methacryloyloxyethyltri methylammonium sulfate)	Poly(methacrylic acid)
Poly(2-hydroxyethyl methacrylate)	Poly(dimethamino ethyl methacrylate)	Poly(maleic acid)
Poly(N-vinyl pyrrolidinone)	Poly(diallyldiethyl ammonium chloride)	Poly(fumaric acid)
Poly(ethylene glycol)	Poly(diethylamino ethyl methacrylate)	Poly(vinylsulfonic acid)
Poly(vinyl alcohol)		Poly(4-vinylbenzoic acid)

2.2.1 Poly(vinyl alcohol)

Poly(vinyl alcohol) (PVA) is the largest volume water-soluble polymer produced today. PVA can not be produced by direct polymerization of the corresponding monomer, due to spontaneous conversion of vinyl alcohol into the enol form of acetaldehyde (Sakurada, 1985; Hay and Lyon, 1967). PVA is attained from the parent homopolymer poly(vinyl acetate) (PVAc).

The polymerization of vinyl acetate occurs via a free-radical mechanism, usually in an alcoholic solution (methanol, ethanol) (Marten and Zvanut, 1992) although for some specific applications a suspension polymerization technique can be used (Sato et al., 1988). PVA is produced on an industrial scale by hydrolysis (methanolysis) of PVAc, often in a one container reactor (Figure 2.2). Different grades of PVA are obtained depending upon the degree of hydrolysis (HD). PVA

grades with HDs 87–89% classified as partially hydrolyzed and 97.5–99.5% as fully hydrolyzed are commercially available. In general, fully hydrolyzed grades of PVA are used mainly in paper coating, in textile warp sizing of hydrophilic fibers and laminating films.

2.2.1 a) Applications of Poly(vinyl alcohol)

Plastic items based on PVA are mainly obtained using solution casting techniques. The researchers in melt processing technology of PVA films need to come with less cost effective casting technologies. However, the main difficulty in PVA thermal processing is the close proximity of its melting point and decomposition temperature. The thermal degradation of PVA in range of 150 to 240ºC, depending on the PVA grades (partially hydrolyzed or fully hydrolyzed). The degradation process gives rise to the release of water from the polymer matrix, accompanied by the formation of volatile degradation products, such as acetic acid in partially acetylated samples (Tsachiya and Sumi, 1969; Yamaguchi and Amagasa, 1961).

Therefore, the thermoplastic processing of PVA at high temperature requires its plasticization with relatively large amounts of organic plasticizers before extrusion. Several suitable PVA plasticizers that capable of enhancing its processibility, such as glycerol (Das et al., 2010), polyethylene glycol (Jansson et al., 2006), and amine alcohols compounds have been proposed and utilized in industrial processes.

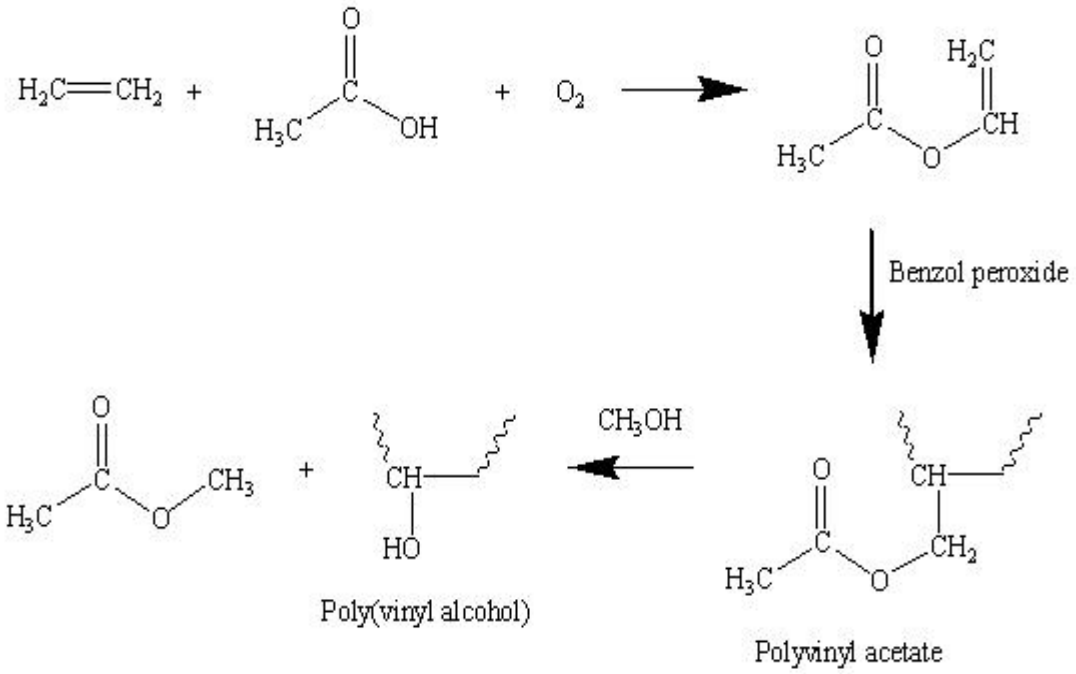

Figure 2.2 Schematic reaction of production PVA in industry (Sakurada, 1985)

2.2.1 b) Biodegradation of Poly(vinyl alcohol)

PVA was found to be the only carbon-carbon backbone polymer that are biodegradable both in aerobic and anaerobic conditions (Chiellini et al., 2003). However, a longer time was required to biodegrade PVA under anaerobic conditions compared to the aerobic conditions (Chiellini et al., 1999; Chiellini et al., 2006b). Furthermore, microorganisms that degrading PVA do not exist in great abundance and are rare such as *Pseudomonas borealis* in soil and *Alcaligenes faecalis* in water (Chiellini et al., 2003). Nevertheless, PVA with different molecular weight (Corti et al., 2002a; and Solaro et al., 2000) and degree of hydrolysis in the range of 80 – 100% (Chiellini et al., 2006b) did not show any significant difference in degradation rate.